Search for indium and thallium based high density scintillators

M. Balcerzyk, Z. Brylewicz, A.Ostrowski, Z. Gontarz, M. Moszy_ski, W.W. Moses, M.J. Weber, S. Derenzo, M. Kapusta, and J. Zachara

***Abstract* - We have studied a set of 8 double oxide compounds of indium and 2 double oxides of thallium. Of these, most indium compounds have density over 6 g/cm^3 and most of thallium compounds have densities over 7 g/cm^3. We have doped them with cerium and terbium. None of them scintillates except for $InTaO_4$:Ce and $InTaO_4$:Tb that scintillate with roughly 4% and 8% of BGO light output respectively. In this paper we report on the reason for choosing indium and thallium compounds, the method of their synthesis and examine the reasons for the lack of scintillation in these compound.**

I. Introduction.

There is a constant need for new high density, high light output scintillators. Fast scintillators are required for Positron Emission Tomography (PET) [1], high light output and low afterglow scintillators are preferred in Computer Tomography (CT) imaging and similar applications [2]. From the existing oxide based scintillators and phosphors Ce doped ones usually have short decay times and Tb doped have usually higher light output [3] than analogous Ce ones. Most recently discovered fast high light output scintillators are double oxides (LSO:Ce – Lu_2SiO_5:Ce, GSO – Gd_2SiO_5:Ce, LuAP:Ce – $LuAlO_3$:Ce, YAP:Ce - $YAlO_3$:Ce, LPS – $Lu_2Si_5O_7$:Ce [4]). Some other are fluorides, bromides, sulfides and chlorides but they usually can be grown as small crystals [5].

Based on crystallographic properties of scintillators and phosphors a simple dependence for light output was formed [6,3]. In short, it connected the difference between shortest of all distances from cation (indium or thallium) to surrounding oxygen ions minus radius of a dopant ion (Ce^{3+} or Tb^{3+}) minus radius of oxygen ion (r_3) with the light output. For highest light output crystals this distance is between 0 pm and –20 pm. The dependence was formulated for yttrium, gadolinium and lutetium cations.

Hitherto new scintillators were developed by substitution of lutetium or gadolinium into yttrium double oxides. In this way the following scintillators were developed: $Y_2(SiO_4)O$ into $Gd_2(SiO_4)O$ and $Lu_2(SiO_4)O$; YPO_4 into $LuPO_4$; $YAlO_3$ into $GdAlO_3$ and $LuAlO_3$. In these compounds the cation mainly contributes to detection efficiency. Anion group of aluminate or silicate have little influence on total cross section for photoelectric effect, which we want to be the highest possible. High density of a compound was caused chiefly by the rare earth ion, which was also the site for a dopant. Presence of SiO_2, Al_2O_3 and P_2O_5 caused lowering of the density of double oxide. Our new approach is based on the idea to govern density of double oxide by the second oxide, *not* the rare earth oxide.

Weber [7] and Zych [8] proposed lutetium and lanthanum tantalates as new scintillators that can be doped with cerium ($LaTaO_4$ {7,8 g/cm^3}, $LaTa_3O_9$ {8,1 g/cm^3}, $LaTa_5O_{14}$ {8,2 g/cm^3}, $LaTa_7O_{19}$ {8,3 g/cm^3}, $LuTaO_4$ {9,8 g/cm^3}, Lu_3TaO_7 {10 g/cm^3}). The physical properties of tantalates are known quite precisely [9] and the Z of tantalum is 73. These compounds exhibit multiexponential scintillations with dominating decay time of tens of ns [7], but the light yield of these compounds is not higher than that of BGO (8200 photons per MeV). The measurements were done on powders and polycrystalline samples.

Since naturally abundant radioactive isotope ^{176}Lu is present at 2.6 mol% concentration in lutetium, scintillators containing this element cannot be used for most nuclear applications requiring large volume of scintillator. Density of a new double oxide material $A_kE_lO_m$ (*k, l, m, n, q, r* are natural numbers, A and E are element names) if not known, can be predicted from molar weight and molar volume of constituent oxides (A_nO_q and E_mO_r). The predicted value is usually lower than the actual one by 3-20%, therefore it can always serve as lower limit for photofraction and upper limit for attenuation length. Based on the light output dependence [3,6] we concluded that double oxides of indium might comprise a new family of high density (≥ 6 g/cm^3) and high light output scintillators. The naturally radioactive isotope ^{115}In has half-life of 4.41_10^{14} years and its abundance in natural indium is 95.7%. Its background β^- (495 keV maximum) decay rate per mol is ca. 316 times lower than in natural lutetium containing radioactive ^{176}Lu. Also thallium +3 double oxides appeared as very high density compounds with photofractions exceeding 35%. From the above mentioned dependence of light output on r_3 it looked that Tl^{+3} compounds ($A_kTl_lO_m$) would have lower light output than the corresponding indium ones ($A_kIn_lO_m$) because Tl^{+3} ionic radius is larger then In^{+3} one.

^{115}In was also interesting for detection of low energy solar neutrinos [10], for which it was first tried as a load to liquid

* Manuscript received October 15, 2000. This work was supported in part by the Polish Committee for Scientific Research, Grant No 8T 11E 025 15

M. Balcerzyk *e-mail: Marcin.Balcerzyk@ipj.gov.pl), M. Moszy_ski and M. Kapusta, are with Soltan Institute for Nuclear Studies, PL-05-400 _wierk-Otwock, Poland,

Z. Brylewicz (zbybryl@chemix.ch.pw.edu.pl), A.Ostrowski, Z. Gontarz and J. Zachara are with Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, PL-00-664 Warsaw, Poland

W.W. Moses (wwmoses@lbl.gov), M.J. Weber and S. Derenzo are with Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA

scintillators [11] and then as a stoichiometric constituent of crystal scintillators like $InBO_3$:Tb [12] and $In_2Si_2O_7$ [13].

The purpose of this work was to synthesize as many as possible In and Tl containing double oxides of high density, to dope them with either Ce or Tb and check for their light output and decay time.

II. Experimental Details.

Table I shows, for all prepared compounds, their density (calculated by the above mentioned method or actual from ICSD database [14]), r_3, 511 keV calculated photofraction [15], attenuation length, color, obtained light output in units of BGO light output (100 is light output of *powdered* BGO) and decay times fitted to scintillation profiles. All compounds were prepared in powder form. All of them were prepared in pure form and when synthesis technology was mastered also doped with either Ce or Tb. Powder pressed pellets of approximate size ∅10mm_1mm were prepared for initial tests. For additional tests 0.2 cm^3 of powder in quartz cuvettes were tested. The intrinsic light output of BGO is 8200 photons/MeV; the observed light output from these powdered samples is lower because of scattering and absorption of emitted light. However, we assume that all the powders have the same scattering and absorption coefficients, allowing us to assume that the ratio of their intrinsic light outputs are the same as the ratio of their observed outputs.

For initial tests we have used a XP2020Q Photonis photomultiplier with a quartz window, custom preamplifier, Tennelec 244 spectroscopy amplifier and Tukan multichannel analyzer. Additional fluorescence lifetime measurements were performed on a pulsed X-ray system [16].

III. Results.

The synthesis of thallium compounds was very difficult since Tl^{+3} easily converts into Tl^{+} charge state, especially in the presence of Ce^{3+}. We have also observed the tendency of In^{3+} reduction into metallic form in the presence of Ce^{3+}.

A. Synthesis of thallium compounds

1) $LaTlO_3$

$LaTlO_3$ was produced in the reaction of lanthanum oxide (III) La_2O_3 with thallium nitride (I) $TlNO_3$. The reaction was undertaken in pipe furnace in air. A uniform mixture of substrates (La_2O_3 + $TlNO_3$) in molar ratio of 1:2 was placed in alundum crucible in the heating zone of the furnace and heated to 600°C at the rate ca. 10°C/min. The reaction took place at that temperature for ca. 3h. After cooling, sample was grounded and again heated in 670°C for 2h. The grinding and heating procedure was repeated 2 or 3 times, up to the moment of removing all substrate materials from the products of reaction. The composition of the material was checked by X-ray phase analysis.

2) $YTlO_3$

$YTlO_3$ was produced in the reaction of yttrium oxide (III)

TABLE I
PROPERTIES OF SYNTHESIZED COMPOUNDS.

Compound	Calculated density, g/cm^3	Experimental density, g/cm^3	r_3, pm	ICSD record #	Calculated 511 keV photofraction	Attenuation length, cm	Color	Obtained light output, powdered BGO=100	Decay time of main component, ns
$InTaO_4$:Tb	7.77	8.21	-20	72569	28.7%	1.09	white	8	32
$InTaO_4$:Ce			-12					4	110
$InGaO_3$:Tb	6.59	6.60	-7	30339	9.3%	1.73	white	1.5	ca. 20
$YInO_3$:Tb	6.01				10.3%	1.88	white	1	
$YInO_3$:Ce								C	
$YInO_3$								B	
$LiInO_2$:Tb		5.87	-8	33954	12.2%	1.92	white	C	
$LiInO_2$:Ce			-17					C	
$CdIn_2O_4$:Tb	6.92	7.13	-4	4118	13.3%	1.54	white	C	
$CdIn_2O_4$:Ce			-13					C	
$BiInO_3$	8.17				38.9%	0.94	white-green	B	
$LaInO_3$	6.8				18.3%	1.56	light brown	B	
$Ba_2In_2O_5$	6.33	6.45		73937	17.3%	1.65	white	B	
$Ba_2In_2O_5$:Ce			-45					B	
$LaTlO_3$:Ce	7.85	8.1	8.7	200088	37.94	0.98	light brown	C	
$LaTlO_3$								C	
$YTlO_3$	7.45				37.2%	1.07	yellowish	B	
$YTlO_3$:Tb								B	

B – count level of background counts from XP2020Q PMT quartz window, C- count level of the quartz cuvette. Experimental densities are taken from ICSD database

Error! Not a valid link.

Fig. 1. Scintillation decay profile for $InTaO_4$:Ce with two exponential fit and quartz cuvette scintillation profile

Y_2O_3 with indium nitride (I) $TlNO_3$ in air. The temperature was set by the results of differential thermal analysis. The reaction products were tested with X-ray phase analysis. The procedure was undertaken in a steel autoclave placed in a zone furnace. A uniform mixture of the substrates (Y_2O_3 + $TlNO_3$ in 1:2 molar ration) was placed in a nickel crucible in a closed autoclave and heated up to ca. 500°C and then kept for ca. 24h. After cooling, the sample was grounded in an agate mortar and again heated in 500°C for 2h. The grinding and heating procedure was repeated 2 or 3 times, up to the moment of removing all substrate materials from the products of reaction. . The composition of the material was checked by X-ray phase analysis.

This synthesis yielded a sintered gray-brown whose X-ray pattern did not agree with any known phase of the Y–Tl–O system. Based on received pattern and analysis of ICSD and ICDD databases we conclude that the received phase is isostructural with $LaTlO_3$. Based on this conclusion elementary cell of yttrium thallate (III) were derived. In an analogous way $YTlO_3:Tb^{3+}$ was produced. Ca. 0.5%mol. of terbium oxalate (III) – $Tb_2(C_2O_4)_3{\cdot}xH_2O$ was added to the substrates.

B. Synthesis of indium compounds

1) $InTaO_4$

The mixture of In_2O_3 (5N), Ta_2O_5 (4N) and $Tb_2(C_2O_4)_3{\cdot}xH_2O$ (5N) or $Ce_2(C_2O_4)_3{\cdot}xH_2O$ (5N) activators were milled for 30 min in an agate mortar to get a uniform mixture. The mixtures were pressed in a platinum crucible, which was subsequently put into a pipe furnace (Heraeus type - Thermicon P). The mixture was sintered in N_2 and the product examined by X-ray phase analysis. It was then heated in an N_2 atmosphere at 1300°C for 2h.

2) $InGaO_3$

The method was the same as in section III.B.1) with substrates In_2O_3 (5N) and Ga_2O_3 (5N) with $Tb_2(C_2O_4)_3{\cdot}xH_2O$ (5N) as activator. It was heated from 20 to 1400°C in an N_2 atmosphere for 2h and then heated in N_2 at 1400°C for 4h.

3) $YInO_3$

The method was the same as in section III.B.1) with substrates In_2O_3 (5N) and Y_2O_3 (5N) with $Ce_2(C_2O_4)_3{\cdot}xH_2O$ or $Tb(NO_3)_3{\cdot}6H_2O$ (5N) as activator. It was heated from 20 to 1500°C in an N_2 atmosphere for 6h and then heated in (H_2/N_2) at 200°C for 2h.

4) $LiInO_2$

The method was the same as in section III.B.1) with substrates In_2O_3 (5N) and Li_2CO_3 (spectpure) with $Ce(NO_3)_3{\cdot}6H_2O$ or Tb_4O_7 (5N) as activator. The heating profile was 20°C to 400°C for 1h in (H_2/N_2) atmosphere, from 400°C to 600°C for 30min., from 600°C to 850°C for 4h, followed by cooling from 850°C to 600°C for 1h in N_2 atmosphere.

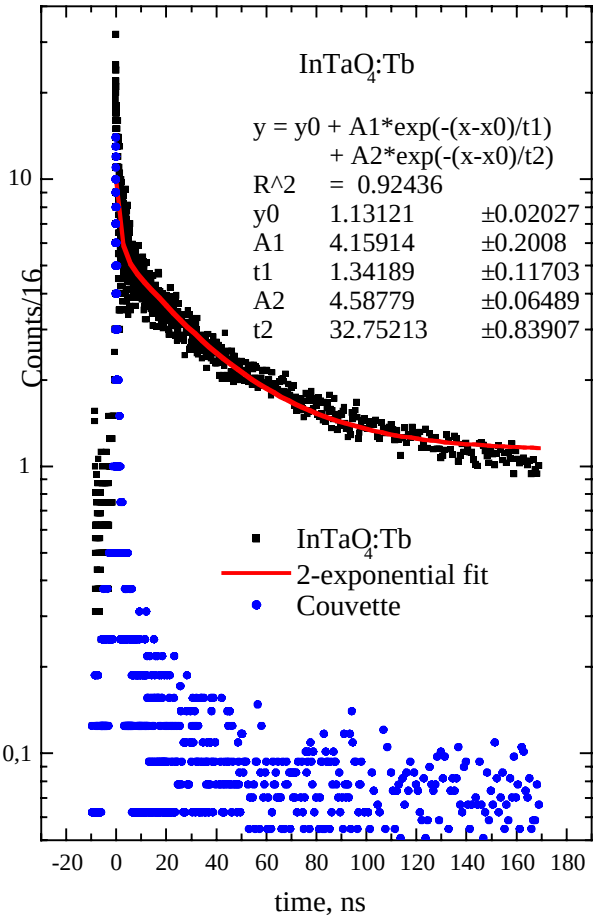

Fig. 2. Scintillation decay profile for $InTaO_4$:Tb with two exponential fit and quartz cuvette scintillation profile

5) $CdIn_2O_4$

The method was the same as in section III.B.1) with substrates In_2O_3 (5N) and $CdCO_3$ (spectpure) with $Tb_2(C_2O_4)_3{\cdot}xH_2O$ (5N) or $Ce_2(C_2O_4)_3{\cdot}xH_2O$ as activator. The mixture was placed directly into furnace of 1000°C for 4h in N_2 atmosphere.

6) $BiInO_3$

The method was the same as in section III.B.1) with substrates In_2O_3 (5N) and Bi_2O_3 (specpure). The heating from 20°C to 1000°C for 1h was applied.

7) $LaInO_3$

The method was the same as in section III.B.1) with substrates In_2O_3 (5N) and La_2O_3 (5N). The heating profile was from 20°C to 1000°C in N_2 atmosphere in 1000°C for 2h. Only an undoped sample was produced.

8) $Ba_2In_2O_5$

The method was the same as in section III.B.1) with substrates of In_2O_3 (5N) and BaO (97%). Heating was done in an oxygen atmosphere: heating from 20 to 400°C for 15 min, heating in. 400°C for 1h, heating from 400°C to 700°C for 30 min, heating from 700 to 900°C for 5h, cooling from 900 to 200°C for 5h. At this time CeO_2 was added and a second heating cycle was applied, heating from 20°C to 1000°C for 3h, heating at 1000°C for 7h and cooling from 1000°C to 200°C for 5h.

C. Light output

The results of light output measurements are shown in the second to last column of Table I. We used the experimental (rather than calculated) density for the attenuation length calculation whenever possible. $InTaO_4$:Tb and $InTaO_4$:Ce showed 8% and 4% of light output of powdered BGO respectively. Other compounds showed lower light output. The scintillation decay profile for $InTaO_4$:Ce with a two-exponential fit and the quartz cuvette scintillation profile are presented in Fig. 1 and the respective ones for $InTaO_4$:Tb in Fig. 2. The decay times are multi-exponential with ca. 110 ns and 32 ns main decay time constants respectively. Since most of the synthesized compounds have white color, we suspect that, for them, the forbidden gap is larger than 3 eV.

IV. Discussion.

It is known that $InBO_3$:Tb and $InBO_3$:Eu are efficient phosphors and have light output of ca. 36000 photons/MeV [17]. Also $In_2Si_2O_7$ is known as a fast intrinsic scintillator with light yield approximately of BGO at 77 K and fast decay time of less then 100 ns [13]. The minimum In-O distance in $InBO_3$ is 215.8 pm [ICSD record 75254], $r_3(Tb^{3+})$ = -9 pm, $r_3(Eu^{3+})$ = -11 pm, $r_3(Ce^{3+})$ = -17 pm. In $In_2Si_2O_7$ the minimum In-O distance is 211.1 pm [18] with the resulting $r_3(Ce^{3+})$ = -22 pm. In $Y_2Si_2O_7$ the minimum Y-O distance is 215.3 pm [ICSD record 28004] with the resulting $r_3(Ce^{3+})$ = -18 pm. It seems that at least some r_3 values listed in Table I fit well into the range of values of efficient indium based scintillators and these listed in [3].

Unfortunately, the efficiencies we have measured for these ten new indium and thallium containing compounds are considerably lower. Although the precise cause is not known we can suggest several possible explanations:

1. The size mismatch between the In^{3+} site and the Ce^{3+} size is too large in some crystallographic lattices to incorporate cerium efficiently. That is probably the case for $InBO_3$ and $Ba_2In_2O_5$ where $r_3(Ce^{3+})$ seems to be too low.
2. The energy gap of double oxides is too narrow to have excited states of a dopant within the band gap. Most 5*d* levels energy of Ce^{3+} listed in [19] have energies above 3.1 eV (400 nm) with the notable exception of garnets. The energy gap of In_2O_3 is 3.6 eV and energy gap of Tl_2O_3 is not precisely known, but since the compound is of a brown color, we suspect it is below 3 eV.
3. The band gap of the double oxide is large enough, but the excited states of the dopant lie within the conduction band, as in Lu_2O_3:Ce [20] and most probably $In_xSc_{1-x}BO_3$:Ce [21]
4. The ground state of the dopant may lie too high within the band-gap to let the dopant collect holes upon ionizing excitation, as in CeF_3 [22]. That is possible since In^{3+} (electronic configuration [Kr] $4d^{10}$) and Tl^{3+} (electronic configuration [Xe] $4f^{14}$ $5d^{10}$) ions do not have closed (s^2p^6) configuration.

We are currently examining other thallium and indium compounds for future scintillators doped with cerium or terbium.

V. References

[1] W. W. Moses and S. E. Derenzo “Scintillators For Positron Emission Tomography”, in: *Proceedings of the International Conference on Inorganic Scintillators and Their Applications SCINT95*, P. Dorenbos, C.W.E. van Eijk. Eds. Delft, Netherlands: Delft University Press, pp. 9-16

[2] W. W. Moses “Scintillator Requirements for Medical Imaging”, proceedings Fifth Int. Conf. on Inorganic Scintillators and Their Applications, SCINT99, August 1999, Moscow, Russia, p. 11-22

[3] M. Balcerzyk, Z. Gontarz, M. Moszynski, M. Kapusta “Future hosts for fast and high light output cerium doped scintillator”, *J. Lumin.* vol.87-89, pp. 963-966, April 2000

[4] D. Pauwels, N. Le Masson, B. Vianna , A. Kahn-Harari, E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk “A novel inorganic scintillator: $Lu_2Si_2O_7:Ce^{3+}$ (LPS)” Paper N7-3, Conference Record of Nuclear Science Symposium 1999, Seatle, USA, 24-30 October 1999, to appear in *IEEE Trans. Nucl. Sci.*

[5] J.C. van't Spijker, P. Dorenbos, C.P. Allier**,** C.W.E. van Eijk, A.R.H.F. Ettema, G. Huber “$Lu_2S_3:Ce^3$, A new red luminescing scintillator.” *Nucl. Instr. Methods B*, vol.134, (Feb. 1998), pp.304-9
and 21 other papers on Cl, Br and F containing scintill ators of C.W.E. van Eijk *et al*. http://www.ipj.gov.pl/~balcerzm/dowziecia/FBrClScintillators.htm

[6] Marcin Balcerzyk “New scintillating materials for γ-ray spectroscopy and detection”, Ph.D. thesis, _wierk Dec. 1997, in Polish http://www.ipj.gov.pl/~balcerzm/dowziecia/PhD/PhDThesisOfMarcinBalcerzyk.pdf

[7] M.J. Weber, S.E. Derenzo, C. Dujardin, W. W. Moses “Dense Ce^{3+} activated scintillator materials” in: *Proceedings of the International Conference on Inorganic Scintillators and Their Applications SCINT95*, P. Dorenbos, C.W.E. van Eijk. Eds. Delft, Netherlands: Delft University Press, pp. 325-8

[8] E. Zych, A. Lempicki, M.J. Downey. "Ce-emission from rare earth tantalate hosts." *Trans Tech Publications. Materials Science Forum,* vol.239-241, 1997, pp.267-70.

[9] F.A. Rozhdestvenskii, M.G. Zuev, A.A. Fotiev *Tantalaty trekhvalentykh metallov* (in Russian), Nauka, Moskwa 1986. See also references in that book.

[10] R.S. Raghavan. "Inverse beta decay of ^{115}In to $^{115}Sn^*$: A new possibility for detecting solar neutrinos from the proton-proton reaction." *Phys. Rev. Lett.*, vol.37, pp.259-62, Aug. 1976

[11] Suzuki Y. Inoue K. Nagashima Y. Hashimoto S. Inagaki T. "Development of indium-loaded liquid scintillators with long attenuation length." *Nucl. Instr. Meth A* vol.293, pp.615-22, Aug. 1990

[12] J. P. Chaminade, A. Garcia, M. Pouchard, C. Fouassier, B. Jacquier, D. Perret-Gallix, L. Gonzalez-Mestres "Crystal growth and characterization of $InBO_3:Tb^{3+}$". *J.Cryst. Growth* vol. 99, pp. 799-804, Jan. 1990

[13] Y. Messous, B. Chambon, M. De Jesus, D. Drain, C. Pastor, A. Garcia, J. P. Chaminade, T. Gaewdang, C. Fouassier, B. Jacquier, B. Varrel "Indium disilicate, a new fast scintillator." *Nucl. Instr. Methods A* vol.354, pp.527-9, Jan. 1995.

[14] Inorganic Crystal Structure Database from FIZ Karlsruhe, Gmelin Institute, Germany, http://www.fiz-karlsruhe.de/pro_serv.html

[15] National Institute of Standards and Technology Program XCOM (Version 1.2) M. J. Berger, 9 MAY 1987, see also web version at http://physics.nist.gov/PhysRefData/Xcom/Text/XCOM.html

[16] S.C. Blankespoor, S.E. Derenzo, W.W. Moses, C.S. Rossington, M. Ito, K. Oba, "Characterization of a pulsed x-ray source for fluorescent lifetime measurements," *IEEE Trans. Nucl. Sci.*, vol. 41, pp. 698-702, Aug. 1994.

[17] R. Raue, AT. Vink, T. Welker "Phosphor screens in cathode-ray tubes for projection television." *Philips Tech. Rev.* vol. 44, p.335, Nov. 1989

[18] G.R. Patzke, R. Wartchow, M. Binnewies "Refinement of the crystal structure of diindium disilicate, $In_2(Si_2O_7$." *Zeitschrift fur Kristallographie-New Crystal Structures*, vol.215, pp.15-16, 2000

[19] P.Dorenbos "The 5d level positions of the trivalent lanthanides in inorganic compounds" *J.Lumin.* vol.91, pp 155-76, Nov. 2000

[20] W.M. Yen, M.Raukas, S.A. Basun, W. van Schaik, U.Happek "Optical and photoconductive properties of cerium-doped crystalline solids" *J. Lumin.* **69**, 287-94, Dec. 1996

[21] T. Gaewdang, J.P. Chaminade, A. Garcia, M. Pouchard, P. Hagenmuller, B. Jacquier "Luminescence of Ce^{3+} in the $In_xSc_{1-x}BO_3$" *J. Phys. Chem. Solids*, vol.55, pp.501-4, June 1994.

[22] C. Pedrini, D. Bouttet, C. Dujardin, A. Belsky, and A. Vasiliev "Energy transfer and quenching process in cerium-doped scintillators" in: *Proceedings of the International Conference on Inorganic Scintillators and Their Applications SCINT95*, P. Dorenbos, C.W.E. van Eijk. Eds. Delft, Netherlands: Delft University Press, pp. 103-110